PCT

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01D 69/14, 67/00	A1	(11) International Publication Number: WO 95/03878
		(43) International Publication Date: 9 February 1995 (09.02.95)

(21) International Application Number: PCT/US94/08642

(22) International Filing Date: 29 July 1994 (29.07.94)

(30) Priority Data:
08/099,684   29 July 1993 (29.07.93)   US

(60) Parent Application or Grant
  (63) Related by Continuation
    US   08/099,684 (CIP)
    Filed on   29 July 1993 (29.07.93)

(71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).

(72) Inventors; and
(75) Inventors/Applicants (for US only): RIES, Paul, D. [US/US]; 4205 Berkshire Court, Midland, MI 48640 (US). MCDONALD, Charles, J. [US/US]; 2915 Oakhaven Court, Midland, MI 48640 (US).

(74) Agent: RUHR, Paula, Sanders; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).

Published
With international search report.

---

(54) Title: COMPOSITE MEMBRANES AND THEIR PREPARATION FROM POLYMER PARTICLES ON A POROUS SUBSTRATE

(57) Abstract

Disclosed is a process of preparing a porous composite membrane by depositing a dispersion of discrete particles on a porous substrate to obtain a composite, and stabilizing the composite. Also disclosed is a porous composite membrane comprising a stable array of partially coalesced particles on the surface of a porous substrate.

COMPOSITE MEMBRANES AND THEIR PREPARATION FROM POLYMER PARTICLES ON A POROUS SUBSTRATE

The present invention relates to a process of
preparing porous composite membranes for ultrafiltration
and microfiltration with particles of polymer on a
porous support and the membranes thereof.

The use of membranes in liquid separation
processes is rapidly growing in the chemical, food,
beverage, electronic, and pharmaceutical industries.
The membranes are becoming increasingly important in
environmental technology such as the recycling of waste
waters in laundry systems.

Ultrafiltration and microfiltration are well
recognized pressure driven processes for liquid
separations. Ultrafiltration and microfiltration
membranes typically have pore sizes that range from
0.001 μm to 10.0 μm. They are often made by processes
that involve phase inversion of a polymer solution
stimulated by temperature or a solvent/non-solvent
combination.

There are a number of problems associated with
currently practiced technology of micro- and
ultrafiltration membranes. In particular, a given
manufacturing process is restricted to limited choice of
surface chemistry and control of pore size. Membrane
performance is accordingly narrowed by these
constraints. A major problem is the flux decline caused
by fouling of the membrane surface. It would be
desirable to improve the versatility and ease of
membrane fabrication to obtain surfaces which would have
reduced fouling tendencies. Such an efficient

fabrication technology would be economical and expand the applications of membrane technology.

It is an object of this invention to utilize the properties of polymer particles to form closely
5   packed structures and develop porous membranes which are easy to prepare, economically attractive; chemically stable; versatile in their application; and which possess desirable thermal, mechanical, and flux properties.
10

It is further an object of this invention to obtain a stable porous composite membrane of uniform structure which is essentially free of cracks; stable to flux; and stable to backflushing and conventional
15 cleaning solutions necessary for a given liquid separation.

It has been discovered that particles of polymers can be deposited on a porous substrate having
20 broad pore size distribution to obtain a composite membrane with a narrower pore size distribution. The interstitial voids between the particles form pores that can discriminate between the solute molecules or
25 particulates for the purpose of carrying out a liquid separation. The composite membranes so obtained are used, for example, as ultrafiltration and microfiltration membranes for liquid separations. As well recognized in the art, such membranes can exist in
30 a variety of configurations such as flat sheet, cassette, spiral wound and hollow fiber modules.

In one aspect, the present invention relates to
35 a process of preparing a porous composite membrane comprising:

a) depositing a dispersion of discrete particles on a porous substrate in one or more steps, whereby a composite with an array of the particles on the substrate is obtained; and

5   b) stabilizing the composite to obtain a composite membrane.

In another aspect, the invention is a porous composite membrane comprising a stable array of
10 particles on the surface of a porous substrate. By stable array, it is meant that the composite membrane is stable to normal operating and cleaning conditions including backflushing.

15   "Discrete particles" as used herein refers to a dispersion of solid organic polymer in a dispersing liquid, or in a continuous medium that is capable of undergoing partial coalescence. The dispersing liquid
20 or the continuous medium is water, or mixtures of alcohol and surfactants, or hydrocarbon. Preferably, the dispersing liquid or the continuous medium is water.

"Partial coalescence" as used herein refers to
25 the ability of the particles of the polymer to adhere to each other and form stable contact points between each other as stimulated by physical and/or chemical means during the fabrication process without filling the interstitial voids between the particles. By forming
30 stable contact points, it is meant that the array of particles is stable with respect to each other and also stable with respect to the porous substrate. Specifically, the composite membrane of this invention
35 is stable to backflushing or conventional cleaning regimes. This means that the composite membrane is not

significantly affected when the liquid flow through the
membrane is reversed as it would be for cleaning.

"Array" as used in this application refers to
the configuration or arrangement of particles on the
5 surface of the porous substrate. In the context of this
application, an array does not necessarily refer to a
perfectly ordered crystalline structure although regions
of short range order likely exist.

10 "Layers" in the array refers to the thickness
of the discriminating layer formed on the porous
substrate. For example, an array having two layers
describes the situation where the statistical average of
the thickness of the discriminating layer corresponds to
15 two times the diameter of the particles making up the
array. Those skilled in the art recognize that the
surface of the porous substrate is generally irregular
and that a two-layer discriminating array may have more
20 or less than the statistical mean number of particles in
any given region.

"Latex" as used herein refers to a dispersion
of particles of polymers in a continuous medium,
25 obtained by emulsion polymerization of the monomers.

The first step in the process of preparing the
composite membrane involves depositing particles on the
surface of a porous substrate. The deposition of the
30 particles may be accomplished by a number of methods
known in the art of coating technology. These methods
include: dipping the substrate in a dispersion of
particles; spraying a dispersion of particles on the
35 substrate; kiss-coating or roll-coating particles on the
substrate; and filtering the dispersion through the

substrate. The deposition of the particles produces an array of particles on the surface. One preferred method of deposition of the particles on the porous substrate is filtration, at atmospheric pressure or under pressure, of the dispersion containing particles through the substrate.

5

In the practice of this invention, it is possible to obtain one or more layers of particles in the array and to have multiple coatings with particles of varying sizes and chemical compositions. The number of layers of the particles in the array may be controlled by varying the concentration of particles in the dispersion for a given surface area of the substrate to be coated. The desired number of layers of particles can be obtained by calculating the mass of coating required for a particular type of packing order of the particles in the array by methods known in the art. The packing order of the particles is discussed below. As an example, assuming a hexagonal close-packed array, for an array with four layers of particles, the mass of coating is calculated to be 0.10 mg/cm^2, 0.30 mg/cm^2, and 0.50 mg/cm^2 with particles having diameters of 0.20 µm, 0.60 µm and 0.90 µm, respectively.

10

15

20

25

The array may vary from about 1 layer of particles to about 1,000 layers of particles in thickness. Preferably, the array is from about 2 layers of particles to about 100 layers of particles in thickness. More preferably, the array is from about 3 layers of particles to about 20 layers of particles in thickness. In general, the number of layers that is most desirable in any given embodiment of the invention will depend on the intended use and on the size of the particles making up the layers. Generally, larger

30

35

particles will result in fewer numbers of layers being used.

It is a particular advantage of the present invention that the averaging effect obtained by multiple layering of the particles significantly minimizes the impact of any defects in the array. By defect is meant discontinuities in the ordering of the particles making them less than perfectly crystalline. This permits composite membranes to be prepared in a commercially practical way. It is not necessary to take additional measures such as slow evaporation of the continuous phase of the dispersion or elimination of emulsifiers in the polymer preparation to obtain a functional membrane with narrow pore size distribution.

The layers of particles which make up the array may be applied simultaneously or sequentially and may be made up of particles of the same size or of different sizes. For example, one or more layers of relatively large particles may be applied to the porous substrate first, and then followed by one or more additional layers of smaller particles. One advantage of this technique is that the larger particles can increase the homogeneity of the porous substrate and facilitate the application of smaller particles. In other situations, layers of particles of the same size may be applied one layer at a time. An advantage of this technique is the preparation of a discriminating layer having minimized defects.

The preparation of the composite membrane generally involves the removal of the dispersing fluid. In the laboratory, the removal of the liquid may be accomplished by placing the composite in a chamber at

about 65 percent relative humidity and allowing it to
dry at ambient temperature or in an oven at elevated
temperatures. In the manufacturing process, the removal
of the dispersing liquid depends on the method employed
for the deposition of the particles on the substrate.

5   In roll-coating of the particles on the substrate, the
removal of the dispersing liquid may be accomplished by
evaporating the liquid at a given temperature depending
upon the nature of the dispersing liquid. Deposition by

10   filtration at atmospheric pressure or under pressure is
particularly facile in removing a substantial amount of
the dispersing liquid during the formation of the array.

The second step in preparing the composite

15   membranes of the invention is stabilization of the
composite. The stabilization of the composite may be
achieved by physical and/or chemical methods. The
stabilization of the composite is necessary to obtain
membranes which are stable, that is, membranes capable

20   of passing water under pressure in either dead-end or
cross-flow mode in either direction with minimal loss of
particles or variation in permeability.

Physical methods of stabilizing the array of

25   the composite involve thermal coalescence of the
particles. The extent of the thermal coalescence of the
particles is a function of the annealing temperature and
the glass transition temperature (Tg) of the particles
or a component polymer in the particles. Particles of

30   crosslinked polymers will be annealed at a higher
temperature than the temperature at which uncrosslinked
polymer will be. For example, a composite with
particles of linear polystyrene annealed at 120°C for

35   about thirty minutes is substantially nonporous with
interstitial voids between the particles filled by the

hydrocarbons, and hydrocarbon derivatives, ketones, and higher alcohols. Preferred plasticizers include di(2-ethylhexyl)phthalate, tricresyl phosphate, acetone, hexane, higher alcohols, and isooctane. The choice of the plasticizer, and the amount of plasticizer used depends upon its compatibility with the polymer or a polymer component of the particle. For example, for polymethylmethacrylate particles, the plasticizer chosen is a polar plasticizer such as acetone or t-butyl alcohol, which may be used in amounts varying from 5 percent to 25 percent by weight of the polymer solids in the dispersion.

Various factors influence the structure of the array and the porosity of the membrane, and consequently, the performance of the composite membrane of the invention. These include the substrate, the composition and morphology of the particles of the dispersion, and the uniformity of structure and degree of order in which the particles are packed.

The substrate materials suitable for this invention include those well known in the art and are commercially available. The substrates may be in the form of flat sheets or hollow fibers. Useful substrates include polysulfone, polyaryl sulfone, polyether sulfone, polyphenyl sulfone, polypropylene, cellulose, polycarbonate, polyphenylene oxide or polyvinyl chloride, Nylon, cellulose nitrate or cellulose acetate-nitrate, interwoven or felted fibers of paper, plastic or glass including filter paper, microporous ceramics, graphite or stainless steel, polyvinylidene fluoride or polytetra-fluoroethylene-co-ethylene, and the like.

coalescing polymer, as evidenced by electron microscopy.
On the other hand, polystyrene particles crosslinked
with about 5 percent by weight of divinylbenzene
coalesce to yield a porous composite. The annealing
temperature can be lowered significantly below the Tg of
5   the polymer of the particle by techniques known to the
art including modifying the surface of the particle with
another polymer with low Tg. Depending upon the
intended use of the composite membrane, the stability,
the mean pore size, and the pore size distribution of
10 the membrane may be controlled by varying the annealing
temperature and the extent of annealing introduced in
the array of the composite.

15   Chemical methods of stabilizing the composite
use a chemical reaction between the particles. The
chemical reaction provides mechanical strengthening or
reinforcement of the contact points between the
particles. An example of the chemical reaction is
20 crosslinking or curing of the particles. This may be
achieved by modifying the surface of the particles by
introducing monomers, having functional groups which are
capable of undergoing crosslinking or curing, during
polymerization in the process of preparing particles.
25 Such monomers are known in the art. Exemplary of the
monomers are glycidyl methacrylate, amide methylol and
the like. Such reactive groups can also be introduced
after the processing of the particles by post-adding
oligomeric or polymeric species to the continuous phase
30 of the dispersion. After formation of the array, these
materials, having adsorbed on the surface of the
particles, can react forming bridging linkages between
the particles during the stabilization step.
35

Another chemical method of stabilizing the
composite may be achieved by swelling the polymer
particles with additional monomer or a mixture of
monomers prior to the placement of the particles on the
5   porous substrate. The amount of monomer or mixture of
monomers used may vary from about 2 percent by weight to
about 150 percent by weight of the particles. The
mixture of monomers may include a monomer with a
functional group capable of crosslinking and a suitable
10 initiator for polymerization. The amount of monomer
with the crosslinking functional groups may vary from
about 1 percent to about 100 percent by weight of the
monomer mixture. The initiator may be chosen from those
known in the art. The amount of the initiator used
15 varies from 0.05 percent to less than 2 percent by
weight of the total weight of the added monomer.
Preferably, the amount of initiator used is from 0.1
percent to 0.50 percent by weight of the total weight of
the added monomer. Thermal initiators useful in the
20 invention include higher alkyl peroxides or azo
compounds, such as, azobisisobutyronitrile and t-
butylperoctoate. Ultraviolet initiators include benzoin
ethyl ether. The array of particles in the composite is
25 exposed to ultraviolet light or heat to initiate
polymerization which results in the adherence of the
particles, and stabilization of the array.

Still another way of inducing stability to the
30 composite is by adding plasticizer to the dispersion of
particles. Plasticizers assist in reducing the
mechanical properties of the polymers such as hardness
and stiffness and Tg of the polymer. Plasticizers may
35 be chosen from a group consisting of phthalate ester,
phosphate esters, fatty acid esters, glycol derivatives,

hydrocarbons, and hydrocarbon derivatives, ketones, and higher alcohols. Preferred plasticizers include di(2-ethylhexyl)phthalate, tricresyl phosphate, acetone, hexane, higher alcohols, and isooctane. The choice of the plasticizer, and the amount of plasticizer used depends upon its compatibility with the polymer or a polymer component of the particle. For example, for polymethylmethacrylate particles, the plasticizer chosen is a polar plasticizer such as acetone or t-butyl alcohol, which may be used in amounts varying from 5 percent to 25 percent by weight of the polymer solids in the dispersion.

Various factors influence the structure of the array and the porosity of the membrane, and consequently, the performance of the composite membrane of the invention. These include the substrate, the composition and morphology of the particles of the dispersion, and the uniformity of structure and degree of order in which the particles are packed.

The substrate materials suitable for this invention include those well known in the art and are commercially available. The substrates may be in the form of flat sheets or hollow fibers. Useful substrates include polysulfone, polyaryl sulfone, polyether sulfone, polyphenyl sulfone, polypropylene, cellulose, polycarbonate, polyphenylene oxide or polyvinyl chloride, Nylon, cellulose nitrate or cellulose acetate-nitrate, interwoven or felted fibers of paper, plastic or glass including filter paper, microporous ceramics, graphite or stainless steel, polyvinylidene fluoride or polytetra-fluoroethylene-co-ethylene, and the like.

The porous substrates generally possess
irregular surfaces with broad pore size distributions.
Consequently, the particles may not only be deposited in
an array on or near the surface but may penetrate the
5   pores and form an array internal to the pores of the
substrate. It is preferred that the particles are
predominantly located in an array on the surface of the
substrate. This may be achieved by proper selection of
the particle size and the pore size of the substrate, by
10   chemical treatment of the substrate and of the
particles, or by adjustments to the coating process such
as using high shear in the coating process or
presaturation of the substrate. Generally, the ratio of
the size of the substrate pore to the size of the
15   particle which is closest to the surface of the porous
substrate is from 0.05 to 7.0. A preferred range is
from 0.3 to 2.0.

It has been discovered that the location of the
20   particles can be controlled conveniently by the
electrostatic interaction between the surfaces of the
particles and the porous substrate, respectively. Thus,
a positively charged substrate provides better retention
and adhesion of particles with an anionic surface.
25   Further in the practice of this invention, the charge of
the substrate can be conveniently controlled by the
adsorption of charged species such as polyelectrolytes
or surfactants. For example, the substrate is coated
30   with a cationic surfactant, dimethyldicocoammonium
chloride to obtain a positively charged substrate,
before the deposition of the anionic particles.
Dimethyldicocoammonium chloride is available under the
35   trade name ARQUAD* from Akzo Chemie America. Examples
of polyelectrolytes include polyacrylic acid,

polymethacrylic acid, polyvinylbenzyl sulfonate, and the like. Generally, any ionic surfactants or polyelectrolytes known in the art are suitable for the purpose of the invention.

5   Particles useful for the purpose of this invention are obtained by dispersion polymerization processes known in the art, such as suspension polymerization, dispersion polymerization and emulsion polymerization. A preferred method of polymerization is 10 emulsion polymerization.

The particles suitable for the purpose of this invention may be made from nonionic monoethylenically unsaturated monomers. The monomers and mixtures of 15 monomers suitable for the purpose of this invention include: monovinyl aromatic monomers; aliphatic conjugated diene monomers; vinylidene halide and vinyl halide monomers; acrylate monomers; and vinyl esters of carboxylic acids containing from 1 to 18 carbon atoms, 20 methacrylonitrile, and acrylonitrile.

Monovinyl aromatic monomers are monomers containing a moiety represented by the formula:

25
$$CH_2 = \overset{\overset{\displaystyle R}{\displaystyle |}}{C} -$$

attached to an aromatic ring containing 6 to 10 carbon 30 atoms. The aromatic ring may be substituted with alkyl or halogen substituents. R is hydrogen or a lower alkyl group having from 1 to 4 carbon atoms. Examples of monovinyl aromatic monomers include styrene, alpha 35

methyl styrene, t-butyl styrene, vinyl toluene, and
halogenated styrenes.

Representative conjugated dienes include
isoprene, 1,3-butadiene, 2-methyl-1,3-butadiene, and
5   other hydrocarbon analogs of 1,3-butadiene.

The acrylate monomers include monovinyl or
divinyl acrylate or methacrylate monomers.
Additionally, acrylate monomers include acids, esters,
10 amides and substituted derivatives thereof. Preferred
monovinyl acrylates are C_1-C_8 alkyl acrylates or
methacrylates. Examples of acrylates include butyl
acrylate, hexyl acrylate, 2-ethyl hexyl acrylate,
t-butyl acrylate, methyl methacrylate,
15 butylmethacrylate, hexylmethacrylate, and
isobutylmethacrylate.

Suitable comonomers useful for the purpose of
this invention are described in U.S. Patents 5,157,071
20 and 5,084,505, which are incorporated herein by
reference.

The surface of the particles of the array
represents the surface of the pores of the composite
25 membrane of the invention. The surface of the particles
may be modified to minimize adsorption of the solutes on
the surface of the pores of the membrane thereby
minimizing the fouling of the membrane in separation
30 technology. Depending upon the chemistry of the solute
mixture or particulate dispersion in the feed solution
used in the separation process, it is possible to design
a membrane starting with particles having appropriate
35 predetermined surface chemistry to minimize the
adsorption of the solutes thereon.

The surface of the particles may be modified by
a number of methods. One of the methods is to
incorporate charged end groups on the surface of the
particle using water soluble initiators in the
5   polymerization process. Another method for modifying
the surface of the particles is to introduce monomers,
which would induce an electrostatic charge and/or
provide a layer of hydrated polymer. These monomers may
be a component of the monomer mixture of the unseeded
10   dispersion polymerization or be introduced into a seeded
dispersion polymerization. Such monomers include, for
example, acrylic acid and/or hydroxyethylacrylate.

Another method for modifying the surface of the
15   particles is to include monomeric or polymeric
surfactants typically known in the art for dispersed
polymerization processes. Typically, the surfactant is
added to the continuous phase of the dispersion. The
amount of surfactant used is an amount sufficient to
20   assist in stabilizing the particles as a colloid, and
minimize contact between particles and prevent
coagulation. The choice of the surfactant and the
concentration of the surfactant varies with the
concentration of the particle solids in the dispersion.
25   The higher the polymer solid level, the higher the level
of surfactant needed. The surfactant may also be chosen
with regard to the nature of the solute mixture or
dispersed particles to be treated in the separation
30   process. An advantage of the present invention is that,
while a wide variety of surfactants or surface active
materials are suitable, it is generally satisfactory to
use readily available conventional surfactants.

35

Typically, the surfactant is selected from
cationic, anionic or non-ionic surfactants and mixtures
thereof. The cationic or anionic surfactants are used
when it is desirable to introduce an electrostatic
charge. Non-ionic surfactants are used when it is
desirable to introduce a hydrated surface layer onto the
particles.

Examples of anionic surfactants include
alkylated diphenyl oxide disulfonates, sodium dodecyl
benzene sulfonates, and dihexylesters of sodium
sulfosuccinic acid. Examples of cationic surfactants
include dimethyldicocoammonium chloride, polypropoxy
quaternary ammonium phosphate, and lauryl dimethylbenzyl
ammonium chloride. Examples of nonionic surfactants
include nonylphenozypoly (ethyleneoxy)ethanols in
various homologous series, ethoxylated alkyl phenols,
and glycerol ethoxylates.

Still another method of modifying the surface
of the particles is to adsorb polymers/oligomers thereon
by techniques known in the art of coating. The
adsorption is achieved by introducing solution
polymers/oligomers into the continuous medium or
dispersing liquid of the dispersion. Suitable
polymers/oligomers include polyelectrolytes and hydrated
polymers. Illustrative of polyelectrolytes include
polymethacrylic acid, polyacrylic acid, polyvinylbenzyl
sulfonate, poly(vinyl pyridinium chloride) and the like.
Illustrative of hydrated polymers include poly
n-vinylamide, poly(n-vinyl-2-pyrrolidone),
polyacrylamide, polyvinylimides and the like.

The particles obtained by dispersion
polymerization processes may have various physical and

compositional morphologies. Compositionally, the
particles may have homogeneous, core/shell,
interpenetrating polymer network or microdomain
morphology. The core/shell particles are characterized
in that the polymer in the interior (core) of the

5   particle is different from the polymer on the surface
(shell) of the particle. There may be more than one
concentric shell in the particle. The surface polymer
thickness or shell thickness may be expressed as the

10   percent of the diameter of the overall diameter. The
core may be predominantly hydrophobic in nature, and the
shell may be hydrophilic in nature with a thin surface
layer of a polymer which would undergo some chemical
reaction which stabilizes the array after formation.

15
     Homogenous morphology is one in which the
polymer or the copolymer is essentially uniform in
composition independent of its location within the
particle.

20
     Interpenetrating polymer network morphology is
one where the particles contain two polymers, each in a
network form.

25   The microdomain morphology is a dispersion of
one polymer within a particle giving rise to surface
heterogeneities which have unique properties,
e.g., adsorption characteristics.

30   A particle morphology having predominantly
polar or hydrophilic polymer on the surface is the
preferred compositional morphology of the particles for
the purpose of this invention.

35   Physical morphology of the dispersed polymer
particles may vary from spherical to nonspherical

depending upon the processing conditions. The
non-spherical particles can have a variety of
morphologies such as multilobed or raspberry-like
structures. With emulsion polymerized particles the
swelling of a crosslinked seed particle with an
5 appropriate amount of monomer prior to the
polymerization is a technique known to the art that
yields particles with non-sperical morphology. The
methods of obtaining particles with different physical
morphologies are taught in Scientific Methods for the
10 Study of Polymer Colloids and Their Application,
F. Candau, and R.H. Ottewill, Kluwer Academic
Publishers, Netherlands, 1990, pps 529-565, relevant
teachings of which are incorporated herein.
15
          Generally, the particles useful in this
invention are spherical in shape and have sizes ranging
from 0.0050 μm to 100.0 μm. It is preferred that the
particle size is 20 μm or smaller.
20
          The permeability of the composite membrane of
the invention is a function of the surface and bulk
porosity of its components. In the discriminating layer
of particles, the surface and bulk porosity are a
25 function of the degree of order in the packing of the
particles in the array. Bulk porosity refers to the
volumetric void volume. Surface porosity refers to the
ratio of void cross-sectional area to the total surface
area of the membrane.
30
          It is known in the art that particles can form
crystalline-like arrangements in the dispersed phase due
to electrostatic repulsion between the particles. The
35 particles can form hexagonal close-packed (HCP) or cubic
close-packed (CCP) or mixtures thereof in the dried

state as evidenced by electron microscopy. The degree
of order in the packing of the particles defines the
size distribution of the interstitial voids between the
particles and the porosity of the array of the
particles. The packing efficiency for HCP and CCP can

5   be calculated by well known techniques described in
J. V. Smith, <u>Geometrical and Structural Crystallography</u>,
John Wiley & Sons, New York, 1982, Chapters 2 and 5; and
H. E. White et al., <u>J. Am. Ceram. Soc.</u>, <u>20</u>, 155, (1937);
and D. Dollimore, G. R. Heal, <u>J. Colloid & Interface</u>

10 <u>Sci.</u> <u>43.</u> 233 (1973), which are incorporated herein by
reference for their teachings.

For CCP, the surface porosity of the array

15 would be 21.5 percent and bulk porosity would be
47.6 percent. For HCP, the surface porosity of the
array would be 9.3 percent and bulk porosity would be
26.0 percent. For a hexagonal close-packed structure,
the pore size of the array is estimated to be about

20 15 percent of the particle size. A structure with a
100 percent uniformity represents the narrowest possible
pore size distribution. The width of the pore size
distribution of the array increases as the disorder in
the packing of the particles increases. Spherical

25 particles ranging in size from 0.0050 μm to 100.0 μm
define a pore size of the membrane from 0.0008 μm to
15.0 μm, based on hexagonal close-packed structure.

The degree of the order in the packing of the

30 particles is dependent upon various factors such as the
kinetics of deposition of the particles, the solids of
the dispersion of the particles, the size of the
particles, the ionic strength of the dispersing medium

35 as determined by the presence of electrolytes and other
ionic materials present therein, and the drying

conditions. The pore size distribution can be
manipulated by selectively blending polymer particles of
various sizes. In the practice of this invention, it is
not necessary that the particles are arranged in a
perfectly uniform structure without a defect. As

5   discussed above, the versatility of the composite
membranes of the invention lies in the fact that it is
possible to selectively obtain an array with multiple
layers of particles. During the separation process, the

10 path a solute takes through the array of the composite
membrane of the invention is tortuous. The multiple
layering of the particles provides statistical averaging
of the pore sizes such that the effect of the defects
within the packing order of the particles on the pore

15 size distribution is minimized.

Figures 1, 2, 3, and 4 illustrate the composite
membranes of the present invention.

20 Figure 1 illustrates the scanning electron
micrograph of the surface of the membrane showing both
the hexagonal and cubic close packing morphology.

Figure 2 illustrates a scanning electron
micrograph of the surface of a particle array obtained

25 by filtration of polystyrene particles with a size of
0.7 μm on to the surface of a polysulfone with a nominal
pore size of 0.2 μm sold under tradename SUPOR⁻ 200 and
commercially available from Gelman Sciences Inc.

30 Figure 3 illustrates a scanning electron
micrograph of the surface of a particle array obtained
by slow drying of the coating of the latex containing

35 polystyrene particles with a size of 0.34 μm on to the
surface of a porous polysulfone with a nominal pore size

of 0.2 μm, sold under tradename SUPOR™ 200 and
commercially available from Gelman Sciences, Inc.

Figures 4 and 5 illustrate scanning electron
micrographs of freeze fractured cross sections of
5   membranes made with 0.16 μm polymethylmethacrylate
particles deposited on a polysulfone substrate with a
nominal pore size of 0.10 μm sold under the tradename
SUPOR™ 100 and commercially available from Gelman
Sciences, Inc. The concentration of the polymer solids
10   in the dispersing liquid was varied to obtain
approximately 4 and 10 layers of particles,
respectively. The packing efficiency estimated from the
scanning electron micrographs is about 40 percent for
the surface porosity and 55 percent for the bulk
15   porosity for both the membranes.

Ultrafiltration and microfiltration membranes
may be characterized in a variety of ways, including
porosity, mean pore size, maximum pore size, bubble
20   point, gas flux, water flux, and molecular weight cut
off. Such techniques are well known in the art for
characterizing microporous membranes. See Robert
Kesting, Synthetic polymer Membranes, 2nd edition, John
25   Wiley & Sons, New York, New York, 1985, pp. 43-64;
Channing R. Robertson (Stanford University), Molecular
and, Macromolecular sieving by asymmetric
ultrafiltration membranes, OWRT Report, NTIS
No. PB35-1577661EAR, Sept. 1984, and ASTM Test Methods
30   F316-86 and F317-72 (1982); the relevant portions of
which are incorporated herein by reference.

Pore size of the membrane may be estimated by
35   several techniques including scanning electron

microscopy, and/or measurements of bubble point, gas
flux, water flux, and molecular weight cut off.

The microfiltration composite membranes of this
invention are characterized in terms of nitrogen flux
5   from 0 to 300 pounds per square inch above the
atmospheric pressure (psig) as determined by ASTM
F316-70. The nitrogen flux of the composite membranes
of the invention is a function of the corresponding flux
of the porous substrate. Generally, the nitrogen flux
10 of the composite membrane is greater than about 0.05
percent and less than about 100 percent of the
corresponding nitrogen flux of the porous substrate,
depending on the size of the particles and the
15 conditions of stabilization.

The mean pore size of the membranes of this
invention useful for microfiltration is preferably
between 0.02 µm and 10 µm, more preferably between
20 0.05 µm and 5 µm; the maximum pore size of such
membranes is preferably less than about 10 µm, more
preferably less than about 8 µm.

The membranes of this invention useful for
25 ultrafiltration are typically characterized by molecular
weight cutoff (MWCO). Molecular weight cutoff is
defined as the smallest molecular weight species for
which the membrane has more than 90 percent retention.
Ultrafiltration membranes, depending upon their pore
30 size distribution, can retain polysaccaride species in
the molecular weight range of 1,000 to 5,000,000.

The mean pore size of the membranes of this
invention useful for ultrafiltration is preferably
35 between 0.0005 µm and 0.10 µm, more preferably between

0.0010 µm and 0.05 µm; the maximum pore size of such membranes is preferably less than about 0.10 µm, more preferably less than about 0.08 µms.

The composite membranes of this invention exhibit a water flux, at about 25°C and about 10 psig, greater than about 0.05 percent and less than about 100 percent of the corresponding water flux of the microporous substrate depending upon the size of the particles and the conditions of stabilization.

The pure water permeability is measured according to the techniques known in the art. The water permeabilities of the composite membranes of the invention are measured with a dead-end stainless steel apparatus. The surface area of the membranes is about 12.5 cm. The pressures applied during the permeability measurements range from 0 to about 60 pounds per square inch above the atmospheric pressure (psig).

Specific Embodiments

The following examples are included for illustrative purposes only and are not intended to limit the scope of the invention or claims. All percentages are by weight unless otherwise indicated. In all the examples that follow, the particle sizes were measured by hydrodynamic chromatography, a technique well known in the art of emulsion polymer characterization.

Example 1 - Preparation of Particles: Microfiltration Membranes

A series of particles made by emulsion polymerization useful in the manufacture of the membrane of this invention are listed in Table I. Their processing involved either a single stage polymerization

or multistage polymerizations in sequence. Table I
described particles of both uniform composition and
structured morphology, e.g., core-shell. Typically,
these polymerizations were carried out in a continuous
addition mode which means a monomer(s) charge and an

5   aqueous initiator charge were introduced as two separate
streams into a 1-gallon jacketed glass reactor equipped
with a mechanical stirrer. The initial aqueous charge
in the reactor typically included a surfactant material,

10 such as the anionic Aerosol MA80 (American Cyanamide,
Stanford CN), introduced at a level to reach the desired
particle size, usually from 0.25 percent to 1 percent
based on monomer(s). The aqueous initiation stream
typically contained 1 percent by weight of sodium

15 persulfate based on the weight of monomer. Prior to
starting the polymerization, the monomer, aqueous
charges, and the initial reactor charge were purged with
nitrogen for thirty minutes. The reactor was maintained
at 70°C and both the aqueous stream of sodium persulfate

20 and the monomer(s) stream were fed continuously for
about 6 hours. The reactor was then heated to about
85°C for about 30 minutes after the additions were
completed. Typically, it was found that substantially

25 all the monomer was converted to polymer giving an
emulsion of from 30 to 50 percent solids depending on
the amounts of monomer(s) added.

The distinction between single stage and
multistage polymerization is that in the latter process

30 there is present a seed latex particle in the initial
reactor charge. It is well known in the art that
successive polymerization using seeds enables
development of particles of large size which cannot be

35 made with classical emulsion polymerization methods in a
single stage polymerization. Typically, in the

development of the particles in Table I, those particles
above 0.34 µm were made in a multistage process. In
some instances, it is desirable to have the seed
particle crosslinked into a network polymer in order to
insure concentric placement of successive polymer

5   shells. Divinylbenzene or allyl methacrylate are
examples of such divinyl monomers useful at levels of 1
to 3 percent based on total monomer charge.

TABLE I

Latex	Particle Size (µm)	Composition	Particle Morphology
1A	0.12	PS/DVB	Homogeneous
1B	0.34	PS/DVB	Homogeneous
1C	0.70	PS/DVB	Homogeneous
1D	0.10	PMMA	Homogeneous
1E	0.21	PMMA	Homogeneous
1F	0.34	PMMA	Homogeneous
1G	0.59	PMMA	Homogeneous
1H	0.69	PS/PMMA	Core/Shell

PS: Polystyrene
PS/DVB: Polystyrene crosslinked with
              divinylbenzene
PMMA: Poly(methyl methacrylate)

Example 2 - Preparation of Particles with a Reactive
              Shell: Microfiltration Membranes

       The stability of the composite membrane of this
invention to backflushing and cleaning can be obtained
by placement of reactive groups on the surface of the
particles such that covalent bonds can be formed at the
surface contact points after positioning the particles
in the array. The particles described in Table II were
made to illustrate this point based on the reaction of

an epoxy group with a carboxylic acid to give a hydroxy
ester linkage. The epoxy groups were introduced into
the shell of the particle by use of glycydyl
methacrylate monomer. Typically, the particles were
placed on the substrate and then heat treated to
5   covalently bond the contact points.

The particle on which the reactive shell was
placed is identified in Table II as 2A. This is a
0.59 μm core-shell latex with polymethyl methacrylate
10 polymerized on a polystyrene seed. The outer shell of
this particle was modified with a crosslinked polymer
containing methyl methacrylate, butyl acrylate, acrylic
acid, ally methacrylate and glycidylmethacrylate. The
thickness, the glass transition temperature of the shell
15 polymer, and the amount and type of reactive species
were varied as described in Table II. The
polymerization of these components on to the surface of
the 0.59 μm seed particle was carried out with
essentially the same procedures as described in
20 Example 1.

25

30

35

TABLE II

Latex	Particle Size (μm)	Outer Shell Composition	Shell Thickness (Å)	Calc. Tg of Shell (°C)
2A	0.59	Core/Shell Polystyrene/- Polymethylmethacrylate		
2B	0.65	MMA(59)/BA(18)/- GMA(16)AMA(4)/AA(4)	206	80
2C	0.64	MMA(76)/- GMA(16)AMA(4)/MAA(4)	200	115
2D	0.66	MMA(75)/BA(18)/- AMA(4)/AA(4)	195	80

MMA: methyl methacrylate
GMA: glycidyl methacrylate
BA: butyl acrylate
AA: acrylic acid
AMA: allyl methacrylate

Examples 3-6

Examples 3-6 illustrate the process of preparing composite membranes of the invention by different methods of deposition of the particles.

Example 3 - Preparation of a Composite Membrane by Gravitational Filtration

A piece of porous polysulfone substrate, 6.2 cm in diameter with a nominal pore size of 0.2 μm, was mounted in a filtration cell (AMICON model 8200). The polysulfone is available under the tradename SUPOR™ 200 from Gelman Sciences, Inc. The substrate was rinsed using 40 g of (1:1) methanol/water solution. A sample of the dispersion of 0.7 μm polystyrene particles of Latex 1C, Table I) was diluted with deionized water to 0.02 percent solids. Fifty grams of the diluted sample

were filtered onto the substrate without the addition of
external pressure. The resulting composite was placed
in a 120°C oven for 5 minutes after which it was
characterized using electron microscopy and gas
permeability data. The membrane had an array, of
5   polymer particles, approximately 4 layers thick,
deposited on the substrate surface with a mean flow pore
size of 0.110 μm.

Example 4 - Preparation of a Composite Membrane by
10   Pressure Filtration

          A 6.2 cm diameter piece of porous polysulfone
substrate (SUPOR™ 200) with a nominal pore size of
0.2 μm, was mounted in a filtration cell (AMICON
15   model 8200). The substrate was rinsed using 40 g of
(1:1) methanol/water solution. A sample of the
dispersion of 0.7 μm polystyrene particles of Latex 1C,
Table I, was diluted with deionized water to
0.02 percent solids. Fifty grams of the diluted sample
20   were filtered onto the substrate with the addition of
5 psig of pressure to the feed side of the filtration
cell. The resulting composite was placed in a 120°C
oven for 5 minutes after which it was characterized
25   using electron microscopy and gas permeability data.
The membrane had an array of polymer particles,
approximately 4 layers thick, deposited on the substrate
surface and a mean flow pore size of 0.147 μm.

Example 5 - Preparation of a Composite Membrane by
30   Using a Meyer Rod

          A 2 inch by 3 inch piece of porous polysulfone
substrate, SUPOR™ 200, with a nominal pore size of
35   0.2 μm was soaked in deionized water for one minute. It
was placed on a glass plate where the excess water was

removed using a rubber roller. A sample of the
dispersion of 0.34 μm polystyrene (Latex 1B, Table I)
was diluted with deionized water to obtain a dispersion
containing 2 percent by weight of solids and 0.5 percent
by weight of alkylated diphenyl sulfonate surfactant
5   available under the tradename DOWFAX 8390 from The Dow
Chemical Company. To this diluted sample was added
8 percent styrene monomer, based on the weight of the
polymer, containing benzoin ethyl ether at 0.1 percent
by weight of styrene and the treated dispersion was
10   placed at one end of the substrate. The substrate was
coated by drawing the dispersion across the surface
using a #4 Meyer rod. The excess dispersion was removed
by blotting it from the glass plate. The sample was
15   then placed in a chamber at approximately 65 percent
relative humidity and allowed to dry at ambient
temperature overnight. The coating was fixed by
exposing it to ultraviolet radiation for twenty minutes.
This membrane had a mean flow pore size of 0.104 μm.
20

Example 6 - Preparation of a Composite Membrane by
              Dip Coating
        A composite membrane was prepared by contacting
one side of SUPOR™ 200 substrate with the surface of
25   the dispersion of Example 5 for about ten seconds before
it was removed and held vertically. The excess
dispersion was blotted from the bottom edge after which
the sample was laid flat, covered, and allowed to dry at
about 65 percent relative humidity and ambient
30   temperature overnight. The coating was fixed by
exposing it to ultraviolet radiation for twenty minutes.
This membrane had a mean flow pore size of 0.096 μm.

35

Example 7 - Stabilization of the Composite Membrane by
                    Thermal Annealing

        Two composite membranes were prepared using the
procedure described in Example 4 except only one of the
membranes was annealed at 120°C for 5 minutes.

        The stability of these membranes was examined
by measuring the mean flow pore size of the composite
membranes, with the particle layer of the composite in
two different orientations with respect to the substrate
and gas flow, namely, upstream and downstream. By
feeding the gas such that the particle array was on the
downstream side, the ability to disrupt the array with
gas flow would be enhanced. By feeding the gas such
that the particle array was on the upstream side thereby
forcing the particles into the substrate would minimize
any disruption to the array. The mean flow pore size,
for the unannealed array with the particle layer located
downstream, was found to be about the same as that of
the uncoated SUPOR™ 200, namely 0.27 µm, indicating the
unfixed coating was unstable. The results are
illustrated in Table III below.

                        TABLE III

Particle Layer Orientation	Mean Flow Pore Size Unstabilized (µm)	Mean Flow Pore Size Thermally Stabilized (µm)
Upstream	0.147	0.167
Downstream	0.223	0.164

Example 8 - Stabilization of the Composite Membrane by
           Chemical Fixation with Monomer

Two composite membranes were prepared. One was
chemically stabilized and the other was not.

5   A 6.2 cm diameter piece of porous polysulfone
substrate (SUPOR™ 200) with a nominal pore size of
0.2 μm, was mounted in a filtration cell, AMICON
model 8200. The substrate was rinsed using 40 g of
10   (1:1) methanol/water solution. A sample of the
dispersion of 0.7 μm polystyrene particles of Latex 1C,
Table I, was diluted with deionized water to 2.0 percent
solids. This sample was treated with 8 percent styrene
based on weight of the polymer solids. The styrene
15   monomer contained 0.1 percent by weight benzoin ethyl
ether. A sample of the treated dispersion was diluted
with deionized water to 0.02 percent polymer solids and
50 g of the resulting dispersion were filtered onto the
substrate with the addition of 5 psig pressure to the
20   feed side of the filtration cell. The resulting
composite was stabilized by exposing it to ultraviolet
radiation for 20 minutes. The membrane was tested for
stability using the procedure described in Example 7.
25   The stability results of the two composite membranes are
illustrated in Table IV below.

30

35

TABLE IV

Particle Layer Orientation	Mean Flow Pore Size Unstabilized (µm)	Mean Flow Pore Size Chemically Stabilized (µm)
Upstream	0.147	0.153
Downstream	0.223	0.159

Example 9 - Modification of the Pore Size and Pore
Size Distribution of the Substrate

A membrane was prepared and stabilized as
described in Example 8. The mean flow pore sizes and
their standard deviation for the composite membrane and
the uncoated polysulfone substrate, respectively, were
measured using the dry/wet gas flow technique. The
results are set forth below in Table V. The composite
membrane had a smaller mean flow pore size and standard
deviation than the polysulfone substrate.

TABLE V

Sample	Mean Flow Pore Size (µm)	Standard Deviation (µm)
SUPOR™ 200 (substrate)	0.27	0.18
Composite	0.146	0.039

Example 10 - Constant Particle Size, Different
Composition

Two membranes, each with a different
dispersion, were prepared. One membrane was prepared

with 0.7 μm polystyrene (PS) particles of Latex 1C,
Table I, in accordance with the process of Example 8
except that the dispersion was treated with 4 percent by
weight of styrene, based on the weight of the solids,
containing 0.1 percent by weight of benzoin ethyl ether,
5 based on the weight of styrene, and diluted to
0.02 percent solids. A second membrane was prepared
with 0.69 μm PMMA/PS particles Latex 1H, Table I, in
accordance with the process of Example 8, except the
dispersion was treated with 4 percent by weight of
10 (MMA), based on the weight of solids, containing
0.1 percent by weight of benzoin ethyl ether, based on
the weight of MMA, and then diluted to 0.02 percent
solids. The mean flow pore sizes and their standard
deviation were measured using gas flow techniques. The
15 results are illustrated in Table VI below. There is no
significant difference in the mean flow pore sizes of
the two membranes.

20

25

30

35

TABLE VI

Particle	Mean Flow Pore Size (µm)	Standard Deviation (µm)
0.7 µm Polystyrene (PS)	0.153	0.035
0.69 µm PMMA/PS	0.146	0.059

Example 11 - Correlation of Pore Size to Particle Size

Two samples of the dispersions of polymethyl methacrylate particles, 0.21 µm (Latex 1E, Table I) and 0.34 µm (Latex 1F, Table I) in diameter, respectively, were prepared as described in Example 1. Each sample was treated with 4 percent by weight of MMA, based on the weight of solids, containing 0.1 percent by weight of benzoin ethyl ether, based on weight of MMA. The samples were then diluted to 0.01 percent and 0.02 percent solids, respectively. Two membranes were then prepared in accordance with the process of Example 8. The mean flow pore sizes and their standard deviation were measured by gas flow techniques. The results are illustrated in Table VII below. The data indicates that smaller particles produced smaller pores.

TABLE VII

Particle Size (µm)	Mean Flow Pore Size (µm)	Standard Deviation (µm)
0.21	0.0570	0.0115
0.34	0.0688	0.0114

Example 12 - Control of Layer Thickness

     A 2 percent solids sample of the dispersion of
0.34 µm polymethyl methacrylate (PMMA) (Latex 1F,
Table I) was treated with 4 percent by weight of MMA,
5 based on the weight of the solids, containing
0.1 percent by weight of benzoin ethyl ether, based on
the weight of MMA. The samples was then diluted to
0.01 percent solids. Two membranes were fabricated
using 49 g and 98 g of the monomer treated dispersion
10 sample in accordance with the process of Example 8. The
mean flow pore sizes and their standard deviation were
measured by dry/wet flow techniques. The results are
illustrated in Table VII below. These data demonstrate
15 that the transport properties of the membrane are
influenced by the thickness of the deposited particle
layer.

TABLE VIII

Amount of Dispersion Applied (g)	Nitrogen Flux at 100 psig Applied Pressure (mL s⁻¹ cm⁻²)	Mean Flow Pore Size (µm)	Standard Deviation (µm)
48	457	0.1391	.0039
98	291	0.1174	.0025

Example 13 - Pure Water Permeability of
Microfiltration Membranes

30   Membranes were prepared with the dispersion of
0.70 µm polystyrene particles of Latex 1C, Table I and
with the dispersion of 0.69 µm core/shell polystyrene-
polymethyl methacrylate PS/PMMA (Latex 1H, Table I)).
35 Membranes were fabricated by using 50 grams of these
dispersions by the filtration technique and stabilized

by the methods described in the previous examples and
listed in Table IX below. In one of the examples,
acetone was used as a coalescing aid, and introduced to
the dispersion prior to filtration of the dispersion
onto the porous substrate. The water permeabilities
5   were measured in a 4 cm diameter dead-end filtration
cell at 5 and 10 psi by the procedures known in the art.
The data for the composite membranes including the
comparative data for SUPOR™ 200 substrate are reported
10 in Table IX below.

15

20

25

30

35

TABLE IX

Particle Type	Particle Size (µm)	Stabilization Method	Water Permeability (mL min⁻¹ cm⁻²)	
			5 psi	10 psi
PMMA-PS	0.67	5 min. at 120°C	8.6	13.0
PMMA-PS	0.67	acetone	8.4, 8.6	16.0, 16.8
PMMA-PS	0.67	acetone/20 min. at 50°C	7.1, 8.3	13.7, 16.2
PMMA-PS	0.67	4 percent MMA, UV	7.6, 7.6	15.0, 14.1
PMMA-PS	0.67	8 percent MMA, UV	7.4	13.8
PS	0.7	4 percent Styrene, UV	6.9	14.5
SUPOR™ 200	--	--	12.0	20.3

Example 14 – Preparation of a Membrane with a Surface
                 Modified Glycidylmethacrylate (GMA Shell
                 Polymer

          A piece of porous polysulfone substrate, 6.2 cm
5   in diameter with a nominal pore size of 0.45 µm was
     mounted in a filtration cell (AMICON Model 8200). The
     polysulfone, SUPOR™ 450, Gelman Sciences Inc., was
     wetted with a (1:1) methanol/water solution after which
     50 ml of a 0.2 percent solution of a cationic
10   surfactant, ARQUAD 2C-75 (Akzo Chemie America, McCook,
     IL) was filtered through the substrate, a fraction of
     which was retained on the surface. The polysulfone was
     flushed using 200 ml of deionized water with 2 psi of
     applied pressure followed by the application of
15   approximately 4 ml of a (1:1) methanol/water solution.
     A 20 percent solids sample of a 0.65 µm latex whose
     shell was modified with GMA (Latex 2B of Table II) was
     diluted to 0.02 percent. The glass transition
     temperature of this reactive shell was calculated to be
20   approximately 80°C. Fifty grams of the diluted sample
     was filtered onto the substrate with the addition of
     2 psi of pressure to the feed side of the filtration
     cell. The resulting composite membrane was placed in an
25   120°C oven for 60 minutes. The thin layer of polymer
     particles was estimated to be 4 layers thick. This
     membrane had a pure water flux of 5.2 (mL min^{-1}cm^{-2}) and
     a mean flow pore size of 0.116 µm.

30   Example 15 – Measurement of Backflushing Stability

          The membrane made in Example 14 was placed in
     the cell described in Example 13 such that the surface
35   coated with particles was positioned downstream relative
     to the water flow on the low pressure side of the cell.

The membrane was initially wetted with a (1:1)
methanol/water solution. The water flux was then
measured from 10 psi to 40 psi transmembrane pressure in
10 psi increments for intervals of 10 minutes. After
each measurement, the pressure was returned to 10 psi,
and the water flux was again measured. The 10 psi flux
was determined to be constant independent of the applied
transmembrane pressures which indicated that the
membrane was essentially stable in this pressure regime.
Elecronmicrographs taken before and after these pressure
treatments indicated no change had occurred in the latex
coating.

Example 16 - Measurement of Membrane Stability to
                    Caustic

Three samples of the membrane prepared in
Example 14 were suspended in a stirred solution of 5.0 N
NaOH at 75°C. The samples were removed at 30, 60 and
120 minutes, respectively, rinsed with deionized water
and allowed to dry at ambient conditions overnight.
Examination by electron microscopy indicated that no
changes had occurred in the deposited surface layer of
particles.

A membrane was prepared using the same
procedure as Example 14 except that the membrane was
dried at 110°C for 60 minutes. This membrane was
mounted in a 10 cm diameter stainless steel crossflow
filtration cell in which a 1.0 N solution of sodium
hydroxide flowed across its surface for 30 minutes at
80°C. The cross-flow rate was 6.5 cm^3/s. The membrane
was removed from the cell, rinsed with deionized water
and allowed to dry at ambient conditions overnight.
Examination of the membrane with electron microscopy

indicated that no change had occurred in the deposited surface layer. Subsequent examination of the water flux of this membrane as described in Example 13 indicated it was constant (10 psi) for 8 hours.

5   Example 17 - GMA Modified Particle: Membrane Stabilized
                     at High Temperature

          A membrane was prepared following the procedures of Example 13 except that the particles from
10   Sample 2C of Table II were used. These particles had a shell polymer with a calculated glass transition temperature of approximately 115°C. Two membranes were made, cured for 1 and 2 hours at 150°C, respectively. The backflushing stability was measured as described in
15   Example 15. The flux at 10 psi was found to be independent of any higher pressures applied up to 40 psi. In addition, the mean pore size before and after the backflushing experiment was measured by gas
20   permeability data as described in ASTM F316-70. These data are in Table X below.

TABLE X

Sample	Heat Treatment	Water Flux – 10 psi (ml min^{-1}cm^{-2})	Mean Pore Size Prior/After Backflushing to 40 psi
1	1 hrs.– 150°C	6.1	0.146 μm/0.148 μm
2	2 hrs.– 150°C	7.3	0.144 μm/0.144 μm

Example 18 - Post-Added Reagent Based Stabilization:
Bisphenol A Diglycidyl Ether

A 20 percent solution of a 0.66 μm latex
modified with a shell polymer containing carboxylic acid
5 (Latex 2D of Table II) was blended with a molar
equivalent of a 100 percent solution of bisphenol A
diglycidyl ether and shaken for 30 minutes. The
membrane was then prepared using the procedures of
Example 14 except that it was placed in an oven for
10 16 hours at 80°C. Measurement of the backflushing
stability as in Example 15 indicated that the 10 psi
water flux was independent of the applied membrane
pressure up to 50 psi. Electronmicrographs obtained on
15 these membranes indicated that the uniformity of the
particle array were independent of the pressure regimes
in these experiments.

Example 19 - Preparation of Particles with a Reactive
20   Shell: Ultrafiltration Membranes

The preparation of the membranes with pore
sizes in the ultrafiltration range, 0.0010 μm to less
than 0.1000 μm requires small particles below about
25 0.2000 μm. Such ultrafiltration membranes were prepared
with the particles listed in Table XI. They were
stabilized with a reactive shell based on the same
chemistry described in Examples 14 and 19. Given the
small size of these particles and the large amount of
30 surface area, the shell thickness is relatively thin
compared to the particles in Table II.

These particles have a core/shell morphology.
35 The seed particles were a crosslinked polymethyl
methacrylate particle (Table XI, latex 11A) with a

diameter of 0.072 μm made in a continuous addition process as described in Example 1. This seed particle was then coated in a subsequent polymerization with the reactive shell identified in Table XI. The calculated glass transition temperature of the shells was 25°C. Four particles with a reactive shell are described in Table XI, each shell having a different thickness. Variation in shell thickness enabled fine control of the size discrimination properties of the ultrafiltration membranes made with these particles (see Example 22).

TABLE XI
Shell Composition

Latex	Particle Size (μm)	Outer Shell Composition	Shell Thickness (Å)
11A	0.072	MMA(99.5)/AMA(0.5	0
11B	0.075	BA(41)/MMA(40)/GMA(15)/AA(3.5)/AMA(0.5)	16
11C	0.081	BA(41)/MMA(40)/GMA(15)/AA(3.5)/AMA(0.5)	40
11D	0.094	BA(41)/MMA(40)/GMA(15)/AA(3.5)/AMA(0.5)	103
11E	0.087	BA(41)/MMA(40)/GMA(15)/AA(3.5)/AMA(0.5)	56

Example 20 - Ultrafiltration Membrane Fabrication

A piece of porous polysulfone substrate, 6.2 cm diameter with a nominal pore size of 0.1 μm was wetted with a methanol/water (1:1) solution and mounted in a filtration cell (AMICON model 8200). The polysulfone is available from Gelman Sciences, Inc. under the tradename SUPOR™ 100. The polysulfone was rinsed with 40 grams of a methanol/water (1:1) solution after which 50 mL of a 0.2 percent solids alcoholic solution (methanol/water

(1:1) of ARQUAD 2C-75 surfactant (Akzo Chemie America;
McCook, IL) was filtered through the substrate. The
polysulfone was flushed using 200 mL of deionized water
with 2 psig of applied pressure followed by the
application of approximately 4 mL of a methanol/water
5   (1:1) solution which was allowed to remain on the
surface. A sample of latex 1D prepared in Example 1 was
treated with ion-exchange resin (BIORAD AG 501-X8). The
treated latex was then diluted to 0.02 percent solids.
Fifty grams of the diluted sample were filtered onto the
10   substrate with the addition of 2 psig of pressure to the
feed side of the filtration cell. The resulting
composite was removed from the filtration cell and
allowed to dry at ambient conditions. The thin coating
15   of polymer particles was estimated to be 8 layers thick.

    An AMICON TCF2 cross-flow cell was used to
examine retention characteristics of the composite
membrane and the SUPOR^{M} 100 substrate. The cross-flow
20   rate was set to 27 mL/min, and a transmembrane pressure
of 5 psig was used. Both the composite membrane and
unmodified substrate were challenged by a 0.01 percent
dextran solution having molecular weights between 9,300
and 7,000,000 daltons. The molecular weight cutoff
25   (MWCO), defined as the mass corresponding to 90 percent
retention of dextran molecules, was determined by
performing size exclusion chromatography on the
permeate. The MWCO of the composite was 300,000 daltons
30   while that of the substrate was greater than 106
daltons.

35

Example 21 - Ultrafiltration Membrane Fabrication:
Multiple Coatings

Following the fabrication method described in
Example 20, two membranes were prepared using latex 11E
5   listed in Table XI of Example 19. The deposited coating
was calculated to be 8 layers thick. A second, thinner
coat (calculated to be approximately 2 layers) of the
same particles was applied to one of the composites by
pressure filtration (2 psig) of the 0.02 percent solids
10 latex. After each coating, the composite membrane was
allowed to dry at ambient conditions.

The retention characteristics of these two
membranes were compared by filtering a 0.01 percent
15 solution of dextrans (9,300-2,000,000 daltons) through
the membranes using the AMICON TCF2 cross-flow cell with
a transmembrane pressure of 5 psig and a cross-flow rate
of 27 mL/min. Table XII compares the two MWCO values
20 obtained from the concentration of dextrans in permeate
samples collected during the first minute of filtration.

Electron micrographs of membranes 1 and 2 of
Table XII indicated that the second coating filled in
25 defects present in the first coating, providing a more
uniform discriminating layer of particles.

TABLE XII

Membrane	Latex	Layers in 1st Coating	Layers in 2nd Coating	MWCO (daltons)
1	11E	8	0	>160,000
2	11E	8	2	32,000

30

35

Example 22 – Effect of Reactive Shell Thickness on
Separation Performance

Multiple coated membranes were prepared, using
latexes listed in Table XI (11B, 11C, and 11D), by the
5   fabrication method described in Example 21. The initial
particle coating was calculated to be 8 layers thick,
and the second, thinner coat was approximately 2 layers.

A 0.004 percent solution of dextrans
10   (9,300-100,000 daltons) was filtered through the
resulting membranes using an AMICON 8050 stirred
dead-end cell with no applied pressure. The MWCO values
obtained from permeate samples collected at 45 minutes
into the filtration are shown in Table XIII. That MWCO
15   values greater than 100,000 daltons can be estimated
results from the polydispersed nature of the 100,000
molecular weight dextran sample.

These data illustrate that the MWCO value is a
20   function of the thickness of the reactive shell,
enabling fine control of the size discrimination of
these membranes.

TABLE XIII

Membrane	Latex	Particle Size (µm)	Shell Thickness (Å)	MWCO (daltons) 45 minutes
1	11B	0.075	16	150,000
2	11C	0.081	40	140,000
3	11D	0.094	103	120,000

Example 23 - Composite Membrane Made by Layering
Particles of Differing Sizes

Multiple coated membranes were prepared, using
latex 1G listed in Example 1 and latex 11E listed in
5   Example 19. The substrate had a nominal pore size of
0.2 μm and is available from Gelman Sciences, Inc. under
the tradename SUPOR⁺ 200. A coating (calculated to be
4.6 layers thick) of 0.59 micron particles (latex 1G)
was applied to the polysulfone substrate as described in
10   Example 20. The resulting composite structure was
stabilized by UV-induced polymerization of MMA (see
Example 9). A second coat (calculated to be 8 layers
thick) of 0.087 micron particles (latex 11E) was applied
to the composite by pressure filtration at 2 psig.
15   After drying at room temperature, a third coat
(calculated to be 8 layers thick) of 0.087 micron
particles was applied in the same way. The resulting
structure was allowed to dry at room temperature.
20

Retention was examined through filtration of a
0.004 percent dextran solution (9,300-100,000 daltons)
under the conditions described in Example 22. Values
for the 90 percent retention mass (MWCO) for samples
25   obtained at 1 and 45 minutes into the filtration are
shown in entry 1 of Table 14. For comparison, data
obtained under the same conditions is shown in entry 2
of Table XIV for the 8+2 layer membrane of Example 22
made with latex 11D. Entries 1 and 2 of Table XVI show
30   the permeate fluxes for these two membranes at 5 and
55 minutes into the filtration of the dextran solution.

These results illustrate how layering particles
35   having different diameters can allow creation of
composite membranes on larger pore substrates, resulting

in increased flux, but similar retention
characteristics.

TABLE XIV

Membrane	Sub-strate	Layers of 0.087 μm Particles	MWCO (daltons) 1 minute	MWCO (daltons) 45 minutes
1	0.2	8 + 8	25,000	91,000
2	0.1	8 + 2	63,000	120,000

Example 24 – Effect of Coating Thickness on Separation Performance

Three multiple coated membranes were prepared
using latex 1G listed in Example 1 and latex 11E listed
in Table XI of Example 19, according to the fabrication
method described in Example 23. In each case, 4.6
layers of 0.59 micron particles (latex 1G) and 8 layers
of 0.087 particles (latex 11E) were applied and
stabilized on a 0.2 μm polysulfone (SUPOR™ 200)
substrate. An additional coating of either 0, 4, or 8
layers of 0.087 micron particles was applied by pressure
filtration (2 psig), and the structure was allowed to
dry.

Retention characteristics were examined as
described in Example 22. The observed molecular weight
cutoff values under these conditions for permeate
samples taken at 45 minutes into filtration are listed
in Table XV. Permeate flux for these membranes during
the filtration of the dextran solution are listed in
Table XVI as entries 2 through 4.

These data illustrate that both MWCO and flux
are influenced by layer thickness.

TABLE XV

Membrane	Layers of 0.087 μm Particles	MWCO (daltons) 45 minutes
1	8 + 0	110,000
2	8 + 4	100,000
3	8 + 8	92,000

TABLE XVI

Membrane	Substrate	Layers of 0.087 μm Particles	Permeate Flux (GFD) 5 Minutes	Permeate Flux (GFD 55 Minutes
1	0.1	8 + 2	60.1	56.5
2	0.2	8 + 8	103.2	93.0
3	0.2	8+4	130.3	115.4
4	0.2	8 + 0	178.1	144.6

WHAT IS CLAIMED IS:

1. A process of preparing a porous composite
membrane comprising:

   a) depositing a dispersion of discrete
       particles on the surface of a porous
       substrate in one or more steps, whereby a
       composite with an array of particles on the
       substrate is obtained; and

   b) using physical or chemical means to
       stabilize the composite to obtain a
       composite membrane.

2. The process of Claim 1, wherein the
particles of the dispersion comprise one or more
polymers.

3. The process of Claim 2 wherein the
composite membrane is stabilized by annealing at a
temperature above the glass transition temperature of a
polymer of the particles.

4. The process of Claim 1, wherein the
composite membrane is stabilized by treating the
particles with a monomer; a surfactant; or an oligomeric
or polymeric material containing functional groups
capable of undergoing chemical reaction.

5. The process of Claim 1, further comprising:
treating the substrate, the particles, or both, by
physical or chemical means to promote deposition of the
particles on the surface of the substrate.

6.   The process of Claim 1, wherein the pore size of the composite membrane is equal to or greater than 0.0008 μm and equal to or less than 15.00 μm.

7.   The process of Claim 1 wherein the particles are deposited on the porous substrate and form an array having more than one layer.

8.   The process of Claim 7 wherein the array consists of layers of particles of different sizes.

9.   The process of Claim 8 wherein the particles in the layer closest to the surface are larger than the particles in subsequent layers.

10. The process of Claim 7 wherein the particles are the same size.

11.   The process of Claim 1 wherein the dispersion of discrete particles is made up of particles having a hydrophilic surface.

12.   A porous composite membrane prepared in accordance with the process of Claims 1 through 11.

13.   A porous composite membrane comprising a stable array of more than one layer of partially coalesced particles on the surface of a porous substrate.

14.   The membrane of Claim 13 wherein the array consists of layers of particles of different sizes.

15.   The membrane of Claim 14 wherein the particles in the layer closest to the surface are larger than the particles in subsequent layers.

16. The membrane of Claim 13 wherein the particles are the same size.

17. The membrane of Claim 13 wherein the dispersion of discrete particles is made up of particles having a hydrophilic surface.

18. The membrane of Claim 13, characterized by a pore size of equal to or greater than 0.0008 μm and equal to or less than 15.00 μm.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   B01D69/14   B01D67/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,89 00592 (BRUNSWICK CORP.) 26 January 1989	1
A	EP,A,0 450 894 (W. L. GORE & ASSOCIATES LTD) 9 October 1991	1
A	FR,A,2 575 398 (NGK INSULATORS, LTD) 4 July 1986	1
A	DE,B,10 47 164 (FARBWERKW HOECHST A. G.) 24 December 1958	
A	FR,A,2 099 183 (MILLIPORE CORP.) 10 March 1972	

☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 October 1994	1 1. 11. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Devisme, F

Form PCT/ISA/210 (second sheet) (July 1992)

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-8900592	26-01-89	US-A-	4855162	08-08-89
		AU-A-	1294288	13-02-89
		CA-A-	1292647	03-12-91
		DE-D-	3888686	28-04-94
		DE-T-	3888686	13-10-94
		EP-A-	0368846	23-05-90
		JP-T-	3501131	14-03-91
EP-A-0450894	09-10-91	GB-A,B	2242431	02-10-91
		JP-A-	6093123	05-04-94
FR-A-2575398	04-07-86	DE-A,C	3546328	03-07-86
		JP-A-	61268314	27-11-86
		US-A-	4874516	17-10-89
DE-B-1047164		NONE		
FR-A-2099183	10-03-72	DE-A-	2116263	05-01-72